

THEORY OF METALLURGICAL PROCESSES

Thermodynamics of Oxygen Solutions in Liquid Ni, Co, Fe, and Mn Metals

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Abstract—Pure gaseous oxygen at a pressure $p_{\text{O}_2}^{1/2} = 1$ is taken as the standard state of oxygen dissolved in a liquid metal. In the case of such a standard state of oxygen, its activity is equal to the equilibrium oxygen partial pressure in the vapor, which is risen to a power of 1/2. This allowed us, using two thermodynamic functions, i.e., the standard Gibbs energy for the oxidation reaction of liquid metal with oxygen to form a lower oxide and the experimentally determined oxygen solubility in a liquid metal, to obtain equations for the energies of mixing of each metal with oxygen and to calculate them, to find linear temperature dependences of the energies of mixing, and to describe oxygen solutions in liquid metals by pseudoregular-solution model equations. Linear dependences of the solubility functions on the standard Gibbs energies for oxidation reactions of liquid metals are found. The aim of the study is to suggest the energies of mixing of four metals (Ni, Co, Fe, and Mn) with oxygen and their temperature dependences for the calculations of the activity coefficients and the activity of oxygen in the solutions of these liquid metals by the pseudoregular-solution model equations.

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1. THEORETICAL ANALYSIS

The feeding of gaseous oxygen to a pure liquid metal results in oxygen dissolution without the formation of metal oxide by the reaction



The reaction equilibrium corresponds to the equality of oxygen chemical potentials in the metal and vapor,

$$\mu_{\underline{\text{O}}} = \frac{1}{2}\mu_{\text{O}_2}. \quad (2)$$

This equality can be expressed using the standard chemical potentials of oxygen $\mu_{\underline{\text{O}}}^\circ$ and $\mu_{\text{O}_2}^\circ$ and second terms $RT\ln a_{\underline{\text{O}}}$ and $RT\ln p_{\text{O}_2}$. The second terms take into account the deviations from the oxygen standard state,

$$\mu_{\underline{\text{O}}}^\circ + RT\ln a_{\underline{\text{O}}} = \frac{1}{2}\mu_{\text{O}_2}^\circ + RT\ln p_{\text{O}_2}^{1/2}. \quad (3)$$

When pure gaseous oxygen at a pressure $p_{\text{O}_2}^{1/2} = 1$ is taken as the standard state of oxygen dissolved in a metal, we have

$$\mu_{\underline{\text{O}}}^\circ = \frac{1}{2}\mu_{\text{O}_2}^\circ$$

and

$$RT\ln a_{\underline{\text{O}}} = RT\ln p_{\text{O}_2}^{1/2}. \quad (4)$$

In the case of such a standard state of dissolved oxygen, its activity in a metal is the equilibrium oxygen partial pressure in the vapor risen to a power of 1/2,

$$a_{\underline{\text{O}}} = p_{\text{O}_2}^{1/2}. \quad (5)$$

At $p_{\text{O}_2}^{1/2} > a_{\underline{\text{O}}}$, oxygen transfers from vapor into a liquid metal by reaction (1) and an increase in the activity and concentration (molar fraction x_{O}) of oxygen in the metal to oxygen solubility $x_{\text{O}_{\text{max}}}$ takes place. At $x_{\text{O}} = x_{\text{O}_{\text{max}}} = \text{const}$, metal oxidation occurs with the formation of the lower oxide by the reaction



Such a sequence of reactions (1) and (6) occurred under equilibrium conditions corresponds to the movement of a figurative point along a conode from pure metal to the liquidus and subsequently across the region corresponding to separation into a metal and its oxide in an $M\text{--O}$ phase diagrams. There are temperature dependences of the standard Gibbs energies for

the oxidation reactions of liquid metals with gaseous oxygen in [1–3],

$$\Delta G_{MO}^{\circ} = A + BT \text{ [J/mol]}. \quad (7)$$

They can be used for the calculation of the equilibrium constants of reactions at a given temperature T ,

$$K_{MO} = \exp\left(-\frac{\Delta G_{MO}^{\circ}}{RT}\right) = \varphi(T). \quad (8)$$

The equilibrium constant of reaction (6) includes the equilibrium activities of metal, its oxide, and oxygen,

$$K_{MO} = \frac{a_{MO}}{a_M p_{O_2}^{1/2}} = \frac{a_{MO}}{a_M a_O}. \quad (9)$$

Oxidation reaction (6) of a pure liquid metal leads to the formation of a pure oxide whose activity is unity, $a_{MO} = 1$. In this case, the expression for the maximum oxygen activity

$$a_{O_{\max}} = \frac{1}{K_{MO} a_M}, \quad (10)$$

follows from Eq. (9), where

$$a_{O_{\max}} = \gamma_{O_{\max}} x_{O_{\max}}, \quad (11)$$

$$a_M = \gamma_M x_M = \gamma_M (1 - x_{O_{\max}}). \quad (12)$$

The oxygen solutions in liquid metals can be adequately described by equations in terms of a regular binary solution model. In accordance with the model, the chemical potentials of the components are related to the energy of mixing of metal and oxygen Q_{M-O} as follows:

$$\begin{aligned} \Delta \mu_M^{\text{exc}} &= RT \ln \gamma_M \\ &= (1 - x_M)^2 Q_{M-O} = x_{O_{\max}}^2 Q_{M-O}, \end{aligned} \quad (13)$$

$$\Delta \mu_{O_{\max}}^{\text{exc}} = RT \ln \gamma_{O_{\max}} = (1 - x_{O_{\max}})^2 Q_{M-O}. \quad (14)$$

The relative chemical potential of a metal expressed through the oxygen solubility and energy of mixing is

$$\begin{aligned} \Delta \mu_M &= RT \ln a_M = RT \ln x_M + RT \ln \gamma_M \\ &= RT \ln (1 - x_{O_{\max}}) + x_{O_{\max}}^2 Q_{M-O}. \end{aligned} \quad (15)$$

The relative chemical potential of oxygen is

$$\begin{aligned} \Delta \mu_{O_{\max}} &= RT \ln x_{O_{\max}} + RT \ln \gamma_{O_{\max}} \\ &= RT \ln x_{O_{\max}} + (1 - x_{O_{\max}})^2 Q_{M-O}. \end{aligned} \quad (16)$$

The relative chemical potential of oxygen also can be expressed from Eq. (10) with allowance for Eq. (15),

$$\begin{aligned} \Delta \mu_{O_{\max}} &= RT \ln x_{O_{\max}} = -RT \ln K_{MO} - RT \ln a_M \\ &= \Delta G_{MO}^{\circ} - RT \ln a_M \\ &= \Delta G_{MO}^{\circ} - RT \ln (1 - x_{O_{\max}}) - x_{O_{\max}}^2 Q_{M-O}. \end{aligned} \quad (17)$$

The right-hand sides of Eqs. (16) and (17) were used to derive an expression for calculating the energy of mixing of a metal and oxygen Q_{M-O} ,

$$Q_{M-O} = \frac{\Delta G_{MO}^{\circ} - RT \ln [x_{O_{\max}} (1 - x_{O_{\max}})]}{x_{O_{\max}}^2 + (1 - x_{O_{\max}})^2}. \quad (18)$$

Since the oxygen solubilities in liquid metals, which are characterized by high affinity to oxygen, are very low ($x_{O_{\max}} \ll 1$), we can assume in a first approximation that $x_M = a_M = 1$. In this case, Eq. (18) can be simplified to a form

$$Q'_{M-O} = \frac{\Delta G_{MO}^{\circ} - RT \ln x_{O_{\max}}}{(1 - x_{O_{\max}})^2}. \quad (19)$$

According to these equations, the energy of mixing depends on the standard Gibbs energy ΔG_{MO}° for the oxidation reaction of a liquid metal with oxygen (6) and oxygen solubility $x_{O_{\max}}$ in this liquid metal. Since $\Delta G_{MO}^{\circ} = A + BT$ and $RT \ln x_{O_{\max}} = aR + bRT$ vary linearly with temperature for each metal and $(1 - x_{O_{\max}})^2 \approx 1$ for metals characterized by low oxygen solubility, the energy of mixing of the metals with oxygen can be conveniently expressed by a linear temperature function

$$Q_{M-O} = C + DT. \quad (20)$$

The binary solutions whose energy of mixing depends linearly on the temperature are called pseudoregular solutions. Therefore, oxygen solutions in liquid metals can be classified among pseudoregular solutions.

2. ENERGIES OF MIXING OF LIQUID Ni, Co, Fe, AND Mn METALS WITH OXYGEN

Table 1 gives oxidation reactions of liquid metals to form liquid lower oxides, the standard Gibbs energies of the reactions $\Delta G_{MO}^{\circ} = f(T)$, and the temperature dependences of the oxygen solubilities in liquid Ni, Co, Fe, and Mn. These metals were used because the oxygen solubilities in them were determined experimentally. The equations given in Table 1 were used to calculate ΔG_{MO}° and $x_{O_{\max}}$ at 1600, 1800, and 2000°C (Table 2). Table 2 also presents the energies of mixing at these temperatures, Q_{M-O} and Q'_{M-O} , which were calculated by Eqs. (18) and (19). At 1600°C, the

Table 1. Reported data on the temperature dependences of the standard Gibbs energies for the oxidation reactions of liquid nickel, cobalt, iron, and manganese and on the oxygen solubilities in these metals

Reaction	$\Delta G_{MO}^{\circ} = A + BT$, J/mol	Reference	$\ln x_{O_{\max}} = -\frac{a}{T} + b$	Reference	$RT \ln x_{O_{\max}}$, J/mol
$Ni_l + 1/2O_2 = NiO_l$	$-210330 + 75.77T$	[1]	$-\frac{17845}{T} + 6.043T$	[1]	$-148360 + 50.24T$
$Co_l + 1/2O_2 = CoO_l$	$-253340 + 81.80T$	[1]	$-\frac{20930}{T} + 7.20T$	[1]	$-174010 + 59.86T$
$Fe_l + 1/2O_2 = FeO_l$	$-239825 + 49.54T$	[1]	$-\frac{14550}{T} + 2.94T$	[4]	$-120970 + 24.44T$
$Mn_l + 1/2O_2 = MnO_l$	$-352420 + 61.67T$	[1]	$-\frac{12572}{T} + 0.267T$	[1]	$-104520 + 2.22T$

Table 2. Energies of mixing of liquid metals and oxygen Q_{M-O} calculated by Eqs. (18) and (19)

System	$t, ^\circ\text{C}$	$x_{\text{O}_{\max}}$	ΔG_{MO}°	$Q_{M-\text{O}}$ (18)	$Q'_{M-\text{O}}$ (19)	$Q'_{M-\text{O}}/Q_{M-\text{O}}$
			kJ/mol			
$\text{Ni}_\text{l}-\text{O}_{\max}-\text{NiO}_\text{l}$	1600	0.0307	−68.41	−14.53	−15.06	1.036
	1800	0.0769	−53.26	−8.94	−10.62	1.118
	2000	0.164	−38.10	−0.76	−5.63	7.41
$\text{Co}_\text{l}-\text{O}_{\max}-\text{CoO}_\text{l}$	1600	0.0187	−100.13	−39.44	−39.63	1.007
	1800	0.0552	−83.77	−36.70	−37.91	1.033
	2000	0.134	−67.41	−34.78	−39.24	1.128
$\text{Fe}_\text{l}-\text{O}_{\max}-\text{FeO}_\text{l}$	1600	0.008	−147.10	−72.88	−73.02	1.002
	1800	0.0174	−137.13	−69.39	−69.71	1.005
	2000	0.0314	−127.22	−65.18	−65.89	1.011
$\text{Mn}_\text{l}-\text{O}_{\max}-\text{MnO}_\text{l}$	1600	0.00159	−236.91	−136.97	−137.00	1.0002
	1800	0.00303	−224.58	−125.34	−125.39	1.0004
	2000	0.00517	−212.24	−113.82	−113.92	1.0009

Q'_{M-O}/Q_{M-O} ratios for all four metals are close to unity; the calculations performed by Eq. (18) and simplified Eq. (19) yield almost identical results. The use of Eq. (17) for nickel and cobalt at 1800°C and, in particular, at 2000°C gives too high Q'_{M-O} magnitudes. Both equations are suitable for calculations for iron and manganese at 1600–2000°C, in which the oxygen solubilities are substantially lower than those in nickel and cobalt.

The metals under consideration belong to the 4th period of the periodic table and are in the following sequence: Ni, Co, Fe, Mn. The values of ΔG_{MO}° and Q_{M-O} change stepwise in the same sequence (see Table 2). The higher the values of $|\Delta G_{MO}^{\circ}|$ along the sequence Ni, Co, Fe, and Mn, the higher the values of the $|Q_{M-O}|$

energies of mixing. The negative deviations of oxygen solutions from the ideal solution increase in the same sequence.

For each metal, the energies of mixing decrease with increasing temperature. The approximation of the temperature dependences of the energies of mixing Q_{M-O} [kJ/mol] with a linear dependence (Eq. (20)) by the least-squares method allowed us to obtain the following regression equations with correlation coefficients r close to unity:

$$Q_{Ni-O} = -79.440 + 0.0344T, \quad r = 0.9942, \quad (21)$$

$$Q_{Co-O} = -60.459 + 0.0114T, \quad r = 0.9958, \quad (22)$$

$$Q_{Fe-O} = -109.055 + 0.0193T, \quad r = 0.9985, \quad (23)$$

$$Q_{Mn-O} = -245.352 + 0.0579T, \quad r = 1.0000. \quad (24)$$

Table 3. Relative chemical potentials of metals (kJ/mol) at the points of oxygen solubility for various temperatures

$RT \ln a_M$	1600 °C	1800 °C	2000 °C
$RT \ln a_{Ni}$	−0.50	−1.43	−3.40
$RT \ln a_{Co}$	−0.31	−0.99	−3.34
$RT \ln a_{Fe}$	−0.13	−0.32	−0.67
$RT \ln a_{Mn}$	−0.03	−0.05	−0.10

3. RELATIVE CHEMICAL POTENTIALS OF METALS AND OXYGEN AT OXYGEN-SOLUBILITY POINTS

The relative chemical potentials of the liquid metals at 1600, 1800, and 2000°C (Table 3) were calculated by Eq. (15) using the oxygen solubilities $x_{O_{max}}$ and energies of mixing Q_{M-O} from Table 2.

It follows from Eq. (17) that the relative chemical potentials of oxygen at points of its solubility consist of terms ΔG_{MO}° and $RT \ln a_M$,

$$\Delta \mu_{O_{max}} = RT \ln a_{O_{max}} = G_{MO}^\circ - RT \ln a_M. \quad (25)$$

At the temperatures under consideration, the values of $|\Delta G_{MO}^\circ|$ for the oxidation reactions of liquid iron and manganese are higher than 100 and 200 kJ/mol, respectively (Table 2). The values of $|RT \ln a_M|$ for saturated oxygen solutions in these liquid metals are several tenths and hundredths of a kilojoule (Table 3). Therefore, term $RT \ln a_M$ in Eq. (25) for the oxygen solutions in iron and manganese can be neglected and we can take

$$RT \ln a_{O_{max}} \approx G_{MO}^\circ. \quad (26)$$

To perform accurate calculations of $RT \ln a_{O_{max}}$ for liquid oxygen solutions in nickel and cobalt at high temperatures, it will be better to use Eq. (25).

4. CHEMICAL AFFINITY OF LIQUID METALS TO OXYGEN AND OXYGEN SOLUBILITIES IN THESE LIQUID METALS

Thermodynamic functions for four liquid metals at three different temperatures (Table 4) were calculated using equations for the temperature dependences of ΔG_{MO}° and $RT \ln x_{O_{max}}$ (Table 1).

An analysis of the values of ΔG_{MO}° and $RT \ln x_{O_{max}}$ shows that, at each temperature, both ΔG_{MO}° and $RT \ln x_{O_{max}}$ increase stepwise in going from Ni to Co, Fe, and Mn. This means that the increase in the affinity of liquid metals for oxygen in the sequence Ni, Co, Fe, and Mn is related to a decrease in the oxygen solubility in the liquid metals according to the same sequence.

The calculated values given in Table 4 were used to plot the dependences of the oxygen solubility functions in liquid metals $RT \ln x_{O_{max}}$ on the standard Gibbs energies ΔG_{MO}° for the oxidation reactions of these metals at three different temperatures (see figure).

The dependences plotted in the aforementioned coordinates are almost linear. Processing the data by least-squares method allowed us to obtain regression equations with correlation coefficients close to unity for each temperature,

$$\text{at } t = 1600^\circ\text{C}, RT \ln x_{O_{max}} = 0.2757 \Delta G_{MO}^\circ - 34.84, \\ r = 0.9997;$$

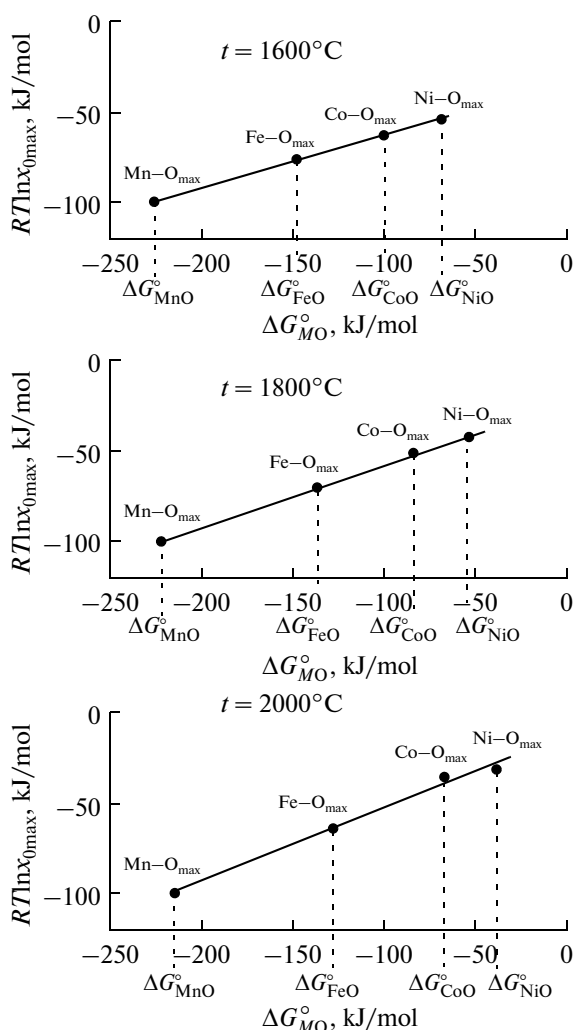
$$\text{at } t = 1800^\circ\text{C}, RT \ln x_{O_{max}} = 0.3344 \Delta G_{MO}^\circ - 24.40, \\ r = 0.9972;$$

$$\text{at } t = 2000^\circ\text{C}, RT \ln x_{O_{max}} = 0.3909 \Delta G_{MO}^\circ - 15.77, \\ r = 0.9945.$$

Thus, for the sequence Ni, Co, Fe, and Mn, we found linear dependences of the oxygen solubility functions for liquid nickel, cobalt, iron, and manganese on the standard Gibbs energies for the oxidation reactions of the metals with gaseous oxygen at several temperatures. This allowed us to extrapolate the obtained dependence for the other metals, such as Cr, V, Ti, Sc, and Ca from the 4th period of the periodic

Table 4. Standard Gibbs energies for the oxidation reactions of liquid metals with the formation of lower oxides and the oxygen solubility functions for the metals at three different temperatures

Reaction	ΔG_{MO}° , kJ/mol			$RT \ln x_{O_{max}}$, kJ/mol		
	1600°C	1800°C	2000°C	1600°C	1800°C	2000°C
$Ni_l + 1/2O_2 = NiO_l$	−68.41	−53.26	−38.10	−54.26	−44.21	−34.16
$Co_l + 1/2O_2 = CoO_l$	−100.13	−83.77	−67.41	−61.89	−49.92	−37.95
$Fe_l + 1/2O_2 = FeO_l$	−147.10	−137.13	−127.22	−75.19	−70.31	−65.42
$Mn_l + 1/2O_2 = MnO_l$	−236.91	−224.58	−212.24	−100.36	−99.92	−99.47



Dependences of the oxygen solubility functions $RT \ln x_{O_{max}}$ for liquid Ni, Co, Fe, and Mn on the standard Gibbs energies ΔG_{MO}° for the oxidation reactions of these liquid metals with gaseous oxygen at 1600, 1800, and 2000°C.

table, in order to estimate the oxygen solubilities in these liquid metals.

CONCLUSIONS

Pure gaseous oxygen at a pressure $p_{O_2}^{1/2} = 1$ is taken as the standard state of oxygen dissolved in a liquid metal. In this case, the oxygen activity in a metallic solution is equal to the equilibrium oxygen partial

pressure in the vapor risen to a power of $1/2$, $a_O = p_{O_2}^{1/2}$. At the point of oxygen solubility in a liquid metal, we have $a_{O_{max}} = p_{O_2(M, MO)}^{1/2}$.

Such a standard state of oxygen allowed us to use available temperature functions (the standard Gibbs energies ΔG_{MO}° for the oxidation reactions of liquid Ni, Co, Fe, and Mn with oxygen with the formation of lower oxides, the oxygen solubilities in these metals) for thermodynamic analysis of oxygen solutions. Equations for relative and excess chemical potentials of metals and oxygen at points of its solubility were used on the assumption that the oxygen solutions in liquid metals can be described adequately by regular and pseudoregular solution models. Equations for the calculation of the energy of mixing of each of the metals with oxygen were derived. Linear temperature dependences of the energies of mixing were obtained.

The metals under consideration correspond to the 4th period of the periodic table and are located in the following sequence: Ni, Co, Fe, and Mn. The values of ΔG_{MO}° , energies of mixing Q_{M-O} , and solubility functions $RT \ln x_{O_{max}}$ vary stepwise according to the same sequence. The higher the values of $|\Delta G_{MO}^{\circ}|$, the higher the values of $|Q_{M-O}|$ and $|RT \ln x_{O_{max}}|$. This means that, in going from one to another metal in this sequence, the negative deviation of the oxygen solutions from an ideal solution increases and the oxygen solubility decreases.

For the sequence Ni, Co, Fe, Mn, linear dependences of the oxygen solubility functions $RT \ln x_{O_{max}}$ on the standard Gibbs energies ΔG_{MO}° for the oxidation reaction of the liquid metals at temperatures of 1600, 1800, and 2000°C were found. This allowed us to extrapolate the obtained dependences to other metals in the 4th period of the periodic table.

REFERENCES

1. I. S. Kulikov, *Deoxidation of Metals* (Metallurgiya, Moscow, 1975).
2. E. T. Turkdogan, *Physical Chemistry for High-Temperature Technology* (Academic Press, New York, 1980).
3. E. A. Kazachkov, *Calculations in the Theory of Metallurgy Processes* (Metallurgiya, Moscow, 1988).
4. *Steelmaking Data Sourcebook* (Gordon Breach Science Publ., New York, 1988).

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